

## **METHOD FOR SYNTHESIZING CARBON NANOTUBES**

### **BACKGROUND OF THE INVENTION**

#### **[0001] 1. Field of the Invention:**

**[0002]** The present invention relates to a method for synthesizing carbon nanotubes through a thermal chemical vapor deposition process, and more particularly to a method for synthesizing carbon nanotubes using magnetic fluid.

#### **[0003] 2. General Background and State of the Art:**

**[0004]** Since carbon nanotubes were first discovered by Iijima in 1991, their specific quantum phenomena occurring at a low dimension due to a quasi-one-dimensional quantum structure have been observed. Particularly, the nanotubes, generally long hollow tubes with an extremely small diameter, were demonstrated to have excellent mechanical strength and chemical stability, and properties of a conductor or a semiconductor depending on their structure. They thus show excellent device characteristics in applications, such as flat panel displays, transistors and energy reservoirs, and are applicable to a variety of nanosize electronic devices. Because of their excellent industrial applicability, research on the carbon nanotubes are being actively conducted.

**[0005]** The carbon nanotubes are broadly divided according to methods and conditions for synthesis into single-layer carbon nanotubes and multi-layer carbon nanotubes of different characteristics. Examples of the method for synthesizing the carbon nanotubes include an arc discharge method and a laser ablation method, which are performed in a laboratory scale, as well as a chemical vapor deposition method and a vapor phase growth method, which are for applying the nanotubes to flat panel displays and nanosize devices.

**[0006]** The arc discharge method, which utilizes an electric discharge device with two electrodes, is a method by which the carbon nanotubes first introduced by Iijima were produced. For arc discharge, two carbon rods with different diameters are used to generate arc. The graphite rods used as the electrodes have high purity and are used as the anode and cathode, respectively. When electric discharge occurs between the two electrodes, carbon clusters detached from the graphite rod used as the anode are condensed on the cathodic graphite rod that is maintained at low temperature. The graphite condensed on the cathode contains carbon nanotubes and carbon nanoparticles. By conducting a purification process to remove the carbon nanoparticles and impurities coexisting with the carbon nanotubes, the carbon nanotubes are collected. In this method, the cathodic carbon rod

generally has a larger diameter than that of the anodic carbon rod which is consumed during an experiment. A reactor tube has a double-wall structure such that cooling water can flow therethrough to cool the carbon nanotubes. The cooling rate plays an important role on the production of the carbon nanotubes. If cooling is insufficient, nanomaterials will be formed at a larger amount than the nanotubes.

**[0007]** In producing the carbon nanotubes by arc discharge, when only carbon rods are used without a transition metal catalyst, multi-layer carbon nanotubes are produced. In this case, after arc discharge, gray-colored hard precipitates are produced on the cathode, in which the multi-layer carbon nanotubes are formed at a soft portion inside the precipitates. On the other hand, when the arc discharge is performed using carbon rods containing a transition metal, single-layer carbon nanotubes are produced. Unlike the multi-layer carbon nanotubes, the single-layer carbon nanotubes are formed at black soot attached throughout the reactor tube. Furthermore, the single-layer carbon nanotubes have significantly different purities according to their produced locations. A portion with the highest purity is the soot attached adjacent to the cathode, 70-90% of which is the single-layer carbon nanotubes. Also, the soot produced on the cathode and the reactor tube wall at the back thereof has the next higher purity. Also, soot, which is produced at large amount but has the lowest purity, is a portion produced within the reactor tube wall. Since the soot is produced in the reactor tube wall at the largest amount, increasing the purity of the soot formed in the reactor tube wall is an important object in synthesizing the single-layer nanotubes using the arc discharge method.

**[0008]** Since the carbon nanotubes synthesized by the arc discharge method contain large amounts of impurities and thus have a lower purity than that of other methods, studies to overcome this problem are being conducted. For the multi-layer carbon nanotubes, the following methods are proposed: a method of rotating the cathode to generate uniform arc (Kukovitsky, E. F. et al., 2000); a method of increasing the temperature of a reactor; a method of using hydrogen gas as a substitute for helium gas (Ando, Y. et al., 2000), and the like.

**[0009]** However, synthesizing the carbon nanotubes using the arc discharge method still shows low yield and necessarily requires a purification process. Also, this method has a problem in that the growth of the carbon nanotubes on a substrate is not possible so that individual nanotubes should be treated and applied.

**[0010]** The laser ablation method, which uses a system for synthesizing only the single-layer carbon nanotubes, allows the production of the carbon nanotubes with very high purity and thus

makes easy the purification of the carbon nanotubes, as compared to other methods. However, this method has the problem of very low productivity.

**[0011]** The chemical vapor deposition (CVD) method is a technology wherein a gaseous raw material containing the desired material is introduced into a reactor in which the raw material is decomposed by heat or plasma energy and the desired material reaches a substrate to form a film. This method for synthesizing the carbon nanotubes using the chemical vapor deposition process comprises depositing a catalytic metal, such as nickel, cobalt or iron, on a substrate in the form of a thin film, decomposing hydrocarbon source gases, such as acetylene, ethylene and methane, by high temperature and plasma, and reacting the decomposed carbon particles with the catalytic metal to synthesize the carbon nanotubes. Thus, this method requires the step of forming a transition metal thin film by a sputtering or evaporation process, before growing the carbon nanotubes, as well as, if necessary, residual treatment processes, such as HF dipping or  $\text{NH}_3$  exposure. The catalytic metal serves as a catalyst of decomposing the raw material gas and also as the nucleation site of the nanotubes.

**[0012]** Examples of the chemical vapor deposition method include hot filament plasma chemical vapor deposition, microwave plasma chemical vapor deposition, and thermal chemical vapor deposition.

**[0013]** In the hot filament plasma chemical vapor deposition method, a tungsten filament that is maintained at a high temperature of about 2,000 °C is mounted just above the substrate, and thus, the hydrocarbon gas is somewhat decomposed via the hot filament section. Thus, this method has an advantage in that the temperature of the substrate can be actually lowered. However, this method has a problem in that it is difficult to uniformly grow the carbon nanotubes on a large-sized substrate.

**[0014]** The microwave plasma chemical vapor deposition method using microwave plasma also allows temperature to be lowered, but has problems in that plasma balls should have large size for large area applications, and the growing carbon nanotubes are exposed to strong hydrogen plasma.

**[0015]** The thermal chemical vapor deposition method comprises forming the carbon nanotubes on a thin film of a catalytic metal, such as nickel, using mainly acetylene or ethylene as raw material gas, and pretreating the surface of the catalytic metal thin film with HF or  $\text{NH}_3$  to facilitate the growth of the carbon nanotubes. In this thermal chemical vapor deposition method, since only one of heating the substrate is used as an energy source for decomposing the raw material gas, there are

advantages in that equipment is easily manufactured, and the carbon nanotubes can be uniformly grown on a large-size substrate if the uniformity of temperature is ensured.

**[0016]** However, in a case where the carbon nanotubes are synthesized using the catalytic metal deposited by a thin film deposition system as in the prior art, there is still the problem of a need for the deposition system, and also the deposition area is limited. Thus, equipment investment is fundamentally required, and equipment investment costs required to increase productivity are rapidly increased. Also, this method allows the deposition of a catalytic metal on the substrate, but has limitations on the mass production of carbon nanotubes. Furthermore, since the catalytic metal must be made into particles for the synthesis of the carbon nanotubes, a process for forming the catalytic metal particles is required. Namely, the producing method according to the prior art is expensive due to equipment investment and the multi-step process.

**[0017]** Meanwhile, in the vapor phase growth method, the process of depositing the catalytic metal is not separately performed, and the carbon nanotubes are synthesized by the decomposition of a gas or liquid source containing the catalytic metal. However, if the source gas containing the catalytic metal component is used, a device for decomposing the source gas will be additionally required. Also, the source gas itself is highly expensive so that the price of the produced carbon nanotubes is increased. Moreover, this vapor phase growth method cannot grow the carbon nanotubes on the substrate so that its applications are limited.

## **SUMMARY OF THE INVENTION**

**[0018]** The present invention has been made to solve the problems occurring in the prior methods for synthesizing the carbon nanotubes, and a first object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the magnetic fluid is used as a catalytic metal so that nano-sized catalytic metal particles are produced at low costs without a need for a thermal pretreatment process as in the case of thin film deposition.

**[0019]** A second object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the amount of iron chloride and ammonium hydroxide is adjusted to control the nanosize of a catalytic metal.

**[0020]** A third object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the amount, times

and timing of addition of a surfactant are adjusted, so that a catalytic metal is uniformly applied on a substrate.

**[0021]** A fourth object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which a catalytic metal is provided on a substrate only by a coating process without using a thin film deposition process, so that the carbon nanotubes are produced at low equipment costs and large amounts.

**[0022]** A fifth object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the produced magnetic fluid is coated on a substrate in admixture with a diluent, such as a binder, to make it possible to uniformly distribute catalytic metal particles on the substrate, and the density of the particles is adjusted depending on the mixing ratio between the magnetic fluid and the binder, to control the distribution and density of the growing carbon nanotubes.

**[0023]** A sixth object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the step of coating a catalytic metal on a substrate is performed in a batch process, and the substrates coated with the catalytic metal are continuously charged into a heating device, so that the carbon nanotubes are produced at increased productivity and large amounts.

**[0024]** A seventh object of the present invention is to provide a method for synthesizing carbon nanotubes using magnetic fluid, in which the synthesized carbon nanotubes have excellent quality such that they can be supplied for the fabrication of samples to be grown on a substrate.

**[0025]** To achieve the first object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the magnetic fluid is used as a catalytic metal.

**[0026]** Particularly, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which magnetic fluid produced from iron chloride is used as a catalytic metal.

**[0027]** More particularly, the catalytic metal, which is used in the inventive method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, is produced by a method comprises the steps of: adding ferrous chloride and ferric chloride to distilled water in a stirring container 11, to produce an aqueous iron chloride solution 13; rotating a stirrer 10 to decompose and mix the aqueous iron chloride solution 13 in the stirring container 11; heating the mixed iron chloride solution with a heating mantle 12 while stirring the solution; adding ammonium

hydroxide to the aqueous iron chloride solution 13 to produce magnetite ( $\text{Fe}_3\text{O}_4$ ) particles; adding a surfactant to the aqueous iron chloride solution 13; adding water and acetone to the aqueous iron chloride solution 13 at room temperature to separate the magnetite particles from liquid of the iron chloride solution 13; and producing a catalytic metal solution with the magnetite particles, distilled water and a binder.

**[0028]** To achieve the second object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the amount of iron chloride and ammonium hydroxide is adjusted such that the nanosize of a catalytic metal is controlled to 10-100 nm.

**[0029]** To achieve the third object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which a fatty acid is used as a surfactant, and added several times with interval such that a catalytic metal is uniformly coated on a substrate.

**[0030]** Particularly, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which  $\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$  is used as the fatty acid, and added alone or in a dissolved state, in several portions such that the catalytic metal is uniformly coated on the substrate.

**[0031]** To achieve the fourth object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which a catalytic metal is coated on a substrate by injecting the catalytic metal on the substrate or dipping the substrate in a catalytic metal solution, without using a thin film deposition process.

**[0032]** Particularly, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which either the catalytic metal is injected and then spin-coated on the substrate, or several substrates are dipped in the catalytic metal solution and then spin-coated with the catalytic metal, so that the catalytic metal is uniformly coated on the substrate by torque.

**[0033]** To achieve the fifth object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the produced magnetic fluid is mixed with a binder and then coated on a substrate, and the amount of addition of the binder is adjusted to control the viscosity of the magnetic fluid such that it does not interfere with the growth of the carbon nanotubes.

[0034] To achieve the seventh object as described above, the present invention provides a method for synthesizing carbon nanotubes using magnetic fluid by thermal chemical vapor deposition, in which the synthesized carbon nanotubes have multiple walls.

[0035] These and other objects of the invention will be more fully understood from the following description of the invention, the referenced drawings attached hereto and the claims appended hereto.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

[0036] The present invention will become more fully understood from the detailed description given herein below, and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein;

[0037] FIG. 1 is a schematic diagram showing a system for producing iron oxide nanoparticles according to the present invention.

[0038] FIG. 2 is a schematic diagram showing a system for the injection and spin-coating of magnetic fluid according to the present invention.

[0039] FIG. 3 is a schematic diagram showing a system for collectively spin-coating magnetic fluid on a large number of substrates according to the present invention.

[0040] FIG. 4 is a SEM photograph (5.0 kV, 13.7 mm x 30.0 k, 1.00  $\mu$ m) showing the surface of the iron oxide particles coated according to Example of the present invention.

[0041] FIG. 5a is a SEM photograph (5.0 kV, 13.9 mm x 30.0 k, 1.00  $\mu$ m) showing the surface of the binder-containing iron oxide particles coated according to Example of the present invention.

[0042] FIG. 5b is a SEM photograph (5.0 kV, 13.9 mm x 80.0 k, 500 nm) showing the surface of the binder-containing iron oxide particles coated according to Example of the present invention.

[0043] FIG. 6a is a SEM photograph (5.0 kV, 13.1 mm x 500, 100  $\mu$ m) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0044] FIG. 6b is a SEM photograph (5.0 kV, 13.3 mm x 1.00 k, 50.0  $\mu$ m) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0045] FIG. 6c is a SEM photograph (5.0 kV, 13.1 mm x 40.0 k, 1.00  $\mu$ m) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0046] FIG. 6d is a SEM photograph (5.0 kV, 13.1 mm x 600, 50.0  $\mu$ m) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0047] FIG. 6e is a SEM photograph (5.0 kV, 12.8 mm x 80.0 k, 500 nm) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0048] FIG. 6f is a SEM photograph (5.0 kV, 12.8 mm x 10.0 k, 5.00  $\mu$ m) showing the carbon nanotubes grown on magnetic fluid according to Example of the present invention.

[0049] FIG. 7a is a SEM photograph (5.0 kV, 12.1 mm x 400, 100  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by a thin film deposition process, according to Comparative Example 1.

[0050] FIG. 7b is a SEM photograph (5.0 kV, 12.7 mm x 1.00 k, 50  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by a thin film deposition process, according to Comparative Example 1.

[0051] FIG. 7c is a SEM photograph (5.0 kV, 11.0 mm x 2.00 k, 20.0  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by a thin film deposition process, according to Comparative Example 1.

[0052] FIG. 7d is a SEM photograph (5.0 kV, 12.3 mm x 80.0 k, 500 nm) showing the carbon nanotubes grown on the Fe thin film deposited by a thin film deposition process, according to Comparative Example 1.

[0053] FIG. 8a is a SEM photograph (5.0 kV, 12.8 mm x 1.00 k, 50.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2.

[0054] FIG. 8b is a SEM photograph (5.0 kV, 12.9 mm x 1.00 k, 50.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2.

[0055] FIG. 8c is a SEM photograph (5.0 kV, 12.9 mm x 3.00 k, 10.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2.

[0056] FIG. 9a is a TEM photograph showing the results of transmission electron microscopy for the carbon nanotubes grown according to an Example of the present invention.

[0057] FIG. 9b is a TEM photograph showing the results of transmission electron microscopy for one strand of the carbon nanotubes grown according to an Example of the present invention.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

[0058] In the present application, “a” and “an” are used to refer to both single and a plurality of objects.

[0059] The main reference numerals in regard to the figures are as follows.



[0060] 10: Stirrer 11: Stirring container

[0061] 12: Heating mantle 13: Aqueous iron chloride solution

[0062] 20: Injector 21: Rotating plate

[0063] 22: Substrate

[0064] Hereinafter, a method for synthesizing carbon nanotubes using magnetic fluid will be described in detail.

[0065] The inventive method for synthesizing carbon nanotubes using magnetic fluid comprises: producing a catalytic metal using magnetic fluid; uniformly coating the produced catalytic metal; and synthesizing carbon nanotubes.

[0066] The magnetic fluid, which is used as the catalytic metal, has a ferrite structure of MO-Fe<sub>2</sub>O<sub>3</sub> in which the position of M can be substituted with various metal components. In the present invention, the position of M has Fe and can be substituted with transition metals, such as Fe, Co and Ni, which are conventionally used as a catalytic metal in a thin film deposition process for allowing the synthesis of the carbon nanotubes. In the present invention, although Fe was used, its modifications, which are obvious to a person having ordinary knowledge in the art, are within the scope of the present invention.

[0067] To produce the catalytic metal particles, the following steps are performed. FIG. 1 is a schematic diagram showing a system for producing an iron oxide nanoparticle-containing catalytic metal solution as the magnetic fluid.

[0068] Step 1: Ferrous chloride and ferric chloride are added to distilled water in a stirring container 11, and uniformly mixed with each other by a stirrer 10 such that they are completely decomposed.

[0069] Step 2: The aqueous iron chloride solution 13 that was uniformly mixed is heated with a heating mantle 12 while stirring the solution.

[0070] Step 3: Ammonium hydroxide is added dropwise to the aqueous iron chloride solution 13 to produce magnetite (Fe<sub>3</sub>O<sub>4</sub>) particles.

[0071] Step 4: A fatty acid is added to the aqueous iron chloride solution 13.

[0072] Step 5: Water and acetone are added to the aqueous iron chloride solution 13 so that the magnetite particles and liquid in the aqueous iron chloride solution are separated from each other.

[0073] Step 6: A catalytic metal solution is produced with the magnetite particles, distilled water, and a binder.

[0074] The produced magnetic fluid has a particle diameter of about 10-100 nm, which varies depending on the amount of iron chloride and ammonium hydroxide. In order to make the magnetic fluid has the above particle diameter, the amount of iron chloride is 1-100g, and the amount of ammonium hydroxide is 1-30 ml. As the amount of iron chloride and ammonium hydroxide is controlled in the above range, the diameter of nanoparticles can be adjusted.

[0075] The fatty acid, which is used in the present invention, is  $\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$ , and added in six portions in which the first portion is added alone and the remaining five portions are added in a state dissolved in acetone.

[0076] As the binder, a ceramic binder is used, and the binder is added at the amount of 0.1-10 g in view of the viscosity of the magnetic fluid.

[0077] The catalytic metal solution produced as described above is coated on the substrate. To coat the catalytic metal solution on the substrate, the present invention utilizes a process of injecting the catalytic metal on the substrate, or a process of dipping the substrate in the catalytic metal solution. However, the present invention is not limited to such processes, and includes coating processes, which can be easily modified by a person having ordinary knowledge in the art.

[0078] In the process of injecting the catalytic metal on the substrate 22, the catalytic metal solution is injected on the substrate placed on a rotating plate 21 by an injector 20 and is uniformly distributed on the substrate 22 by rotational centrifugal force. The rotational speed of the rotating plate is 100-5,000 rpm. If the rotational speed is out of this range, the effect of uniformly coating the catalytic metal solution cannot be achieved.

[0079] In the process of dipping the substrate 22 in the catalytic metal solution, several substrates 22 are bound and dipped in the catalytic metal solution, after which they are placed on the rotating plate 21 and collectively spin-coated with the catalytic metal solution, so that several substrates 22, which were uniformly coated with the catalytic metal, are produced simultaneously. The rotational speed of the substrates is 100-5,000 rpm, and if the rotational speed is out of this range, the effect of uniform coating cannot be achieved.

[0080] The substrate having the magnetic fluid uniformly coated thereon is charged into a heating device for the synthesis of carbon nanotubes, and then, acetylene, ammonia and hydrogen, as source gases, are introduced into the heating device. In the heating device, carbon nanotubes with high density are vertically aligned and synthesized on the substrate at a temperature of 800-900 °C.

[0081] In the processes of producing the catalytic metal using the magnetic fluid, uniformly coating the produced catalytic metal, and synthesizing the carbon nanotubes, the process of

uniformly coating the produced catalytic metal is performed in a batch process where the substrates 22 are spaced from each other at a given interval and coated with the catalytic metal. Also, before the substrates 22 are charged into the heating device, the temperature within the heating device is increased to high temperature allowing the synthesis of the carbon nanotubes. The coated substrates 22 are continuously charged into the heating device having a high temperature atmosphere allowing the synthesis of the carbon nanotubes, and this process is continuously repeated to synthesize the carbon nanotubes at large amounts.

**[0082]** Hereinafter, a preferred example of the present invention will be described in detail with reference to the accompanying drawings. However, the present invention is not limited to or by the example, and various modifications to the example can be embodied without departing from the appended claims. Also, the example is given to more fully illustrate the present invention and to make easy the practice of the present invention by a person having ordinary knowledge in the art.

## **EXAMPLES**

**[0083]** **EXAMPLE** – 0.86 g of ferrous chloride ( $\text{FeCl}_2$ ) and 2.35 g of ferric chloride ( $\text{FeCl}_3$ ) are dissolved in 40 ml of water, and then heated to 80 °C with stirring, to give an aqueous iron chloride solution 13. 5 ml of ammonium chloride ( $\text{NH}_4\text{OH}$ ) is added dropwise to the aqueous iron chloride solution 13 and left to stand for 5 minutes, to produce black magnetite ( $\text{Fe}_3\text{O}_4$ ) powders. The produced magnetite powders are placed on a rotating plate 21 by an injector 20, and uniformly coated on a silicon substrate 22 by torque.

**[0084]** 5.5 g of fatty acid  $\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$  as a surfactant is added to the aqueous iron chloride solution 13. In order to allow the catalytic metal to be uniformly coated, the surfactant is added in such a manner that 0.5 g of the first portion dissolved in 25 ml of acetone is added and then 1 g of each of the remaining five portions, which were dissolved in 50 ml of acetone, respectively, is added. This fatty acid addition technology for allowing the catalytic metal to be uniformly coated is not limited by this Example, and its modifications, which are obvious to a person having ordinary skill in the art, are within the scope of the present invention.

**[0085]** The produced magnetic fluid has a particle diameter of about 10-100 nm, which varies depending on the amount of iron chloride and ammonium hydroxide. To make the magnetic fluid has this particle diameter, the amount of iron chloride is 1-100 g, and the amount of ammonium hydroxide is 1-30 ml.

[0086] The nanosize metal particles, which can be obtained only through a thermal treatment process if the prior thin film deposition process is used, could be formed only by the production of the iron oxide powders according to this Example. FIG. 4 is a SEM photograph (5.0 kV, 13.7 mm x 30.0 k, 1.00  $\mu$ m) showing the surface of the iron oxide particles coated according to this Example. As can be seen in FIG. 4, the particles with uniform size are uniformly distributed.

[0087] When the coating of the produced iron particles is performed on the substrate 22, a binder is added in order to uniformly coat the iron particles by torque and to avoid a phenomenon where the metal particles are locally conglomerated upon heating.

[0088] As the binder, a ceramic binder is used at the amount of 0.75 g per 25 ml of the produced magnetic fluid. Although the binder may also be used at a smaller amount than this amount, it should be added at the amount of at least 0.1 g in order to achieve the effect of uniformly coating the catalytic metal particles. If it is used at an amount exceeding 10 g, it will cause a great increase in viscosity of the catalytic metal so that the growth of the carbon nanotubes can be adversely affected.

[0089] If the iron particles containing the binder is coated, the distribution of the particles will become good, and this uniform coating of the iron particles allows the uniform and high-density growth of the carbon nanotubes.

[0090] The binder is generally removed by the heat applied upon carbon nanotube synthesis as a final step, and has no effect on the synthesis of the carbon nanotubes.

[0091] FIG. 5a is a SEM photograph (5.0 kV, 13.9 mm x 30.0 k, 1.00  $\mu$ m) showing the surface of the substrate 22 coated with the iron oxide particle solution containing the binder, according to this Example, and FIG. 5b is a SEM photograph (5.0 kV, 13.9 mm x 80.0 k, 500 nm) showing the surface of the substrate 22 coated with the iron oxide particle solution containing the binder.

[0092] The substrate 22 coated with the iron particles is charged into a heating furnace, and then maintained at 900 °C under a hydrogen atmosphere. After ammonia gas flows through the heating furnace for 5 minutes, a mixture of ammonia and acetylene gases is introduced into the heating furnace to grow the carbon nanotubes on the substrate 22.

[0093] FIG. 6a is a SEM photograph (5.0 kV, 13.1 mm x 500, 100  $\mu$ m) showing the carbon nanotubes grown on the magnetic fluid according to this Example; FIG. 6b is a SEM photograph (5.0 kV, 13.3 mm x 1.00 k, 50.0  $\mu$ m) according to this Example; FIG. 6c is a SEM photograph (5.0 kV, 13.1 mm x 40.0 k, 1.00  $\mu$ m) showing the carbon nanotubes grown on the magnetic fluid according to this Example; FIG. 6d is a SEM photograph (5.0 kV, 13.1 mm x 600, 50.0  $\mu$ m) showing the carbon nanotubes grown on the magnetic fluid according to this Example; FIG. 6e is a

SEM photograph (5.0 kV, 12.8 mm x 80.0 k, 500 nm) showing the carbon nanotubes grown on the magnetic fluid according to this Example; and FIG. 6f is a SEM photograph (5.0 kV, 12.8 mm x 10.0 k, 5.00  $\mu$ m). As can be seen in FIGS. 6a to 6f, the carbon nanotubes are vertically grown on the substrate 22 at high density.

**[0094]**     Comparative Example 1

**[0095]**     A catalytic metal, which is necessarily required for the synthesis of carbon nanotubes on the catalytic metal deposited by the prior thin film deposition process, was deposited to a thickness of 60 nm using a sputter thin-film deposition equipment, and the synthesis of carbon nanotubes on the deposited catalytic metal was attempted. FIG. 7a is a SEM photograph (5.0 kV, 12.1 mm x 400, 100  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by the thin film deposition process according to Comparative Example 1; FIG. 7b is a SEM photograph (5.0 kV, 12.7 mm x 1.00 k, 50  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by the thin film deposition process according to Comparative Example 1; FIG. 7c is a SEM photograph (5.0 kV, 11.0 mm x 2.00 k, 20.0  $\mu$ m) showing the carbon nanotubes grown on the Fe thin film deposited by the thin film deposition process according to Comparative Example 1; and FIG. 7d is a SEM photograph (5.0 kV, 12.3 mm x 80.0 k, 500 nm) showing the carbon nanotubes grown on the Fe thin film deposited by the thin film deposition process according to Comparative Example 1.

**[0096]**     Comparative Example 2

**[0097]**     Ni particles with a diameter of about 20 nm were purchased and coated on a silicon substrate, and then the synthesis of carbon nanotubes was attempted. FIG. 8a is a SEM photograph (5.0 kV, 12.8 mm x 1.00 k, 50.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2; FIG. 8b is a SEM photograph (5.0 kV, 12.9 mm x 1.00 k, 50.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2; and FIG. 8c is a SEM photograph (5.0 kV, 12.9 mm x 3.00 k, 10.0  $\mu$ m) showing the carbon nanotubes grown on the nanosize Ni particles according to Comparative Example 2.

**[0098]**     In order to examine the structural characteristics of the carbon nanotubes synthesized by Example of the present invention, transmission electron microscopy (TEM) was performed. FIG. 9a is a TEM photograph showing the results of transmission electron microscopy for the carbon nanotubes grown according to Example of the present invention; and FIG. 9b is a TEM photograph showing the results of transmission electron microscopy for one strand of the carbon nanotubes grown according to Example of the present invention. The transmission electron microscopic results

showed the carbon nanotubes with multiple walls were synthesized. This indicates that the carbon nanotubes synthesized by Example of the present invention has a similar quality to that of Comparative Example 1 or 2.

**[0099]** Furthermore, in order to examine if the mass production of the carbon nanotubes is possible, the amount of the carbon nanotubes synthesized per unit area of the substrate 22 was measured. When the carbon nanotubes were synthesized by Example of the present invention, the carbon nanotubes could be synthesized at the amount of 1 g per 80-cm<sup>2</sup> area of the substrate 22. Thus, the carbon nanotube synthesis can be continuously performed and a large number of the substrates 22 can be simultaneously used for the carbon nanotube synthesis.

**[00100] Effect of the Invention**

**[00101]** The present invention is characterized by using the magnetic fluid as the catalytic metal in synthesizing the carbon nanotubes by thermal chemical vapor deposition. Thus, the present invention requires neither the thermal pretreatment process as in the case of thin film deposition nor a separate system for catalytic metal deposition. Also, the present invention allows the nanosize catalytic metal to be produced at low costs and large amounts.

**[00102]** Furthermore, the inventive method for synthesizing the carbon nanotubes by thermal chemical vapor deposition comprises adjusting the amount of iron chloride and ammonium hydroxide to control the nanosize of the catalytic metal, and adjusting the amount, times and timing of the surfactant to uniformly coat the catalytic metal on the substrate 22. Also, the present invention includes coating the produced magnetic fluid on the substrate 22 in admixture with a diluent, such as a binder, so as to allow uniform distribution of the catalytic metal particles on the substrate, and adjusting the density of the catalytic metal particles according to the mixing ratio between the particles and the binder. As a result, the present invention makes it possible to control the distribution and density of the growing carbon nanotubes.

**[00103]** Moreover, in the inventive method for synthesizing the carbon nanotubes by thermal chemical vapor deposition, the catalytic metal is coated on the substrate 22 only by a coating process without a need for a thin film deposition process. This eliminates limitations on the size of the substrate 22, reduces equipment investment costs, and makes possible the mass production of the carbon nanotubes.

**[00104]** Furthermore, according to the inventive method for synthesizing the carbon nanotubes by thermal chemical vapor deposition, the step of coating the catalytic metal on the substrate 22 is performed in a batch process without limitations on the size of a batch. Also, a large number of the

substrates 22 can be used simultaneously, and the steps of coating the catalytic metal and synthesizing the carbon nanotubes can be performed in a continuous process. Thus, the inventive method shows increased productivity and allows the cost-effective mass production of the carbon nanotubes.

**[00105]** In addition, the present invention allows the uniform growth and synthesis of the carbon nanotubes having high quality, such that the synthesized carbon nanotubes can be supplied for the manufacture of a sample to be grown on a substrate.

**[00106]** Although the present invention has been described with reference to the above-mentioned preferred example, those skilled in the art will appreciate that various modifications or changes are possible, without departing from the scope and spirit of the invention. Thus, the accompanying claims will include such modifications or changes within the scope of the present invention.

**[00107]** All of the references cited herein are incorporated by reference in their entirety.

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**[00108]** Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention specifically described herein. Such equivalents are intended to be encompassed in the scope of the claims.